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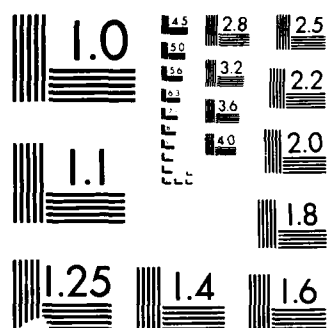
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This international symposium focused on the nonlinear optical properties of organic molecules and conjugated polymers, an exciting area of research clearly at the fore front because of the tremendous interest in optical signal processing and optical computing. This multidisciplinary symposium had participation from theoretical, physical and synthetic chemists, physicists and device engineers. It provided a forum for people from different backgrounds to interface their findings, to review the status of this area from microscopic understanding at one end, to device fabrication at the other end, and to formulate future directions. *Engineering* ←

The symposium highlighted, large nonresonant nonlinear optical effects in organic systems, subpicosecond response times of their optical nonlinearity (both derived from  $\pi$ -electron interactions), high optical damage threshold, and molecular engineering of novel structures and molecular assemblies for enhancing optical nonlinearity. Reported work on molecular engineering dealt with films and fibers, synthesis of new materials, Langmuir-Blodgett films, and electric field poled molecular assemblies.

Theoretical studies dealt with both nonlinear optical properties and electrical conductivity in extended  $\pi$ -electron systems. Several studies included semiempirical calculations of molecular hyperpolarizabilities, both  $\beta$  and  $\gamma$ .

**AFOSR-TR. 88-0487**

FINAL REPORT

PROJECT: Symposium on Electroactive Polymers,  
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State University of New York at Buffalo  
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Copies of the abstracts of the talks presented in chronological order are enclosed. This symposium was very well attended and produced lively discussions on technical matters.

MONDAY AFTERNOON - SECTION A - SYMPOSIUM ON ELECTROACTIVE  
POLYMERS - COSPONSORED WITH THE DIVISION OF POLYMER CHEMISTRY  
(CONTINUED) - D.R. Ulrich, Presiding

10. ELECTROACTIVE POLYMERS -- AN OVERVIEW.  
D.R. Ulrich.

(Abstract not available at time of publication.)

11. NONLINEAR OPTICS: ORGANIC AND POLYMER SYSTEMS. A. F. Garito, Department of  
Physics, University of Pennsylvania, Philadelphia, PA 19104.

Organic and polymer structures exhibit unusually large, ultrafast second and third order nonlinear optical properties that are important to the fields of nonlinear optics and optical device technologies. These properties have been demonstrated in a large number of structures, phases and states that include organic crystals and films, conjugated polymers, monomolecular films, liquid crystals, liquid crystal polymers, polymer glasses, and, more recently, high performance ordered polymers. Significant advances in fundamental understanding have been achieved through experimental and theoretical studies of important electronic mechanisms responsible for these nonlinear optical responses, especially the primary role of highly charge correlated  $\pi$ -electron excited states. The results of these studies will be reviewed by proceeding from ordered to partially ordered assemblies of conjugated molecular and polymer systems that are defined by their respective orientational distribution functions.

12. DESIGN, ULTRASTRUCTURE, AND DYNAMICS OF NONLINEAR OPTICAL EFFECTS IN POLYMERIC THIN FILMS; P. N. Prasad, Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214.

This talk will cover three aspects of my research program at Buffalo: (i) Design of the films of organic macromolecular systems rich in  $\pi$ -electrons. Molecular manipulation is used to control chemical design, ultrastructure, mixed phase fabrication and the film thickness. Interfacial processes such as Langmuir-Blodgett method, electrochemical polymerization and gas-solid interface reactions are used to fabricate films of thicknesses from monomolecular to several microns. (ii) Ultrastructure of these films. We investigate chemical structure, conformation and domain structure by a variety of spectroscopic techniques suitable for thin films. (iii) Nonlinear optical interactions. Results will be presented from our picosecond and subpicosecond four wave mixing experiments to discuss the nature of third-order nonlinear optical processes in these thin films. Surface plasmon coupling and optical wave guiding have been used to investigate nonlinearities of monolayer and multilayer films. Device concepts based on nonlinear properties of polymer films will also be presented.

13. NON LINEAR ORGANIC CRYSTALS FOR PARAMETRIC AMPLIFICATION AND SAMPLING SPECTROSCOPY (PASS)  
I. LEDOUX, J. BADAN, J.L. OUDAR and J. TISS  
CNRS - 196 Av. Henri Ravera 92220 BAGNEUX-FRANCE  
D. MULIN, A. NIGUS and A. ANTONETTI, CNRS 91120 PALAISEAU-FRANCE

A new technique is presented for the subpicosecond sampling and parametric amplification of weak infrared (from 0.8 to 1.6  $\mu$ m) luminescence signals. It depends on the availability of an efficient nonlinear organic crystal such as MPP

(N-(4-nitrophenyl)-(L)-prolinol). A CPM laser (100 fs duration at 620 nm, 1 mJ per pulse) triggers through 1.5 mm of MPP a gain of  $10^4$ . The ultrafast amplification explores in time the luminescence duration at a given wavelength. Phase and group-velocity matching in MPP together with its  $d_{31}$  coefficient ( $200 \cdot 10^{-9}$  e.s.u.) account for its efficiency. PASS is demonstrated in various semiconductor samples and a new I.R. source made of a CPM laser pumped continuum emitting water cell and two MPP crystals is shown to emit powerful tunable subpicosecond pulses.

14. ELECTRIC-FIELD POLING OF NONLINEAR OPTICAL POLYMERS. C. S. WILLAND, S. E. Peth, M. Scoszarava, D. J. Williams, Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650, G. D. Green, J. I. Weinshenk, H. K. Hall, J. E. Mulvaney, Department of Chemistry, University of Arizona, Tucson, AZ 85721

It is well known that conjugated organic systems often display large molecular second-order hyperpolarizabilities. Currently there is only limited use of these systems in devices based on second-order nonlinear optical effects as the materials are required to be noncentrosymmetric. Various methods are being explored for producing acentric materials. Among these, electric-field poling of nonlinear optically active molecules contained in a host medium has been shown to produce substantial macroscopic nonlinearities. This talk will focus on the role of polymers in enhancing molecular alignment in electric fields. Results from solution second-harmonic generation measurements using model monomer and polymer systems will be discussed.

68. FREQUENCY AND TEMPERATURE VARIATION OF CUBIC SUSCEPTIBILITY IN  
POLYDIACETYLENES. P.-A. Chollet, F. Kajzar, J. Messier - CEA/IRDI  
CEN.SACLAY - DEIN/LERA - 91191 Gif-sur-Yvette Cedex - France

Polydiacetylenes are known to exhibit large polarizabilities enhanced by one dimensional  $\pi$ -electron delocalisation and excitonic character of electronic excitation. Third harmonic generation (THG) and electric field induced second harmonic generation (EFISHG) experiments have been carried out on polymer thin films prepared by different techniques (Langmuir-Blodgett, dipping out from polymer solutions, vacuum deposition) and having different conjugation length, at variable incident photon energy and temperature. Two and three photon resonance enhancement in THG and two photon resonance on even and odd parity levels in EFISHG are observed in near IR. Their origin and possible practical repercussion will be discussed. A well pronounced dependence of cubic susceptibility with conjugation length is observed. The excitonic character of cubic hyperpolarizability is studied by THG measurements in function of temperature. Internal polarization is measured by EFISHG.

69. FEMTOSECOND DEPHASING IN A POLYDIACETYLENE FILM MEASURED BY DEGENERATE FOUR-WAVE  
MIXING WITH INCOHERENT NANOSECOND LASER. T. Kobayashi and T. Mottori, Department  
of Physics, University of Tokyo, Hongo, Tokyo 113, Japan

There has been much interest in the dynamical properties of excited states in polydiacetylenes (PDA's). The dephasing time ( $T_2$ ) in PDA's has been studied by several groups, but they could not resolve  $T_2$ . We could for the first time resolve the dephasing time in a PDA (poly-3BCMU) film. It has been shown that one can obtain very short resolution time by using broad-band (incoherent) light in dephasing measurements by degenerate four-wave mixing (DFWM). In our experiment, a broad-band dye laser pumped by a  $N_2$  laser was used for the incoherent light source, and DFWM signals diffracted in two directions were simultaneously detected to obtain resolution times shorter than the correlation time (about 100 fs) of the incoherent light. With the observed peak shifts, 30 and 90 fs at 648 and 582 nm respectively, dephasing times are calculated to be 30 fs at 648 nm and 130 fs at 582 nm. The mechanism which gives the difference in dephasing times will be discussed.

70. STUDIES OF MONOMER AND POLYMER MONOLAYERS USING OPTICAL SECOND AND THIRD HARMONIC  
GENERATION. G. Berkovic and Y. R. Shen, Department of Physics, University of  
California, Center for Advanced Materials, Lawrence Berkeley Laboratory, Berkeley,  
California 94720.

Optical second harmonic generation (SHG) is a highly surface sensitive technique for studying ultrathin molecular layers. We have used this technique to study monolayers of various organic monomers and their corresponding polymers spread at air/water interfaces. The SHG from a water surface covered with a monolayer of vinyl stearate (or octadecyl methacrylate) was much larger than that from a pure water surface. After the monolayer was polymerized by uv irradiation, the SHG decreased to a value identical with that obtained from a monolayer of authentic (bulk polymerized) polymer on water. In collaboration with P. W. Prasad, monolayer polymerization of diacetylenes was also studied by SHG, as well as by third harmonic generation (THG). Although THG, unlike SHG, is not a surface specific probe, the extremely high third order nonlinearity of polydiacetylenes has enabled us to observe for the first time THG from a single monolayer. Methods of calculating molecular nonlinear coefficients from monolayer SHG will be discussed. This work supported by DOE under Contract No. DE-AC03-76SF00098.

71. DEVELOPMENT OF POLYMERIC NONLINEAR OPTICAL MATERIALS. R.N. DeMartino,  
E.W. Choe, D. Haas, G. Khanarian, T. Leslie, G. Nelson, J. Stamatooff,  
D. Stuetz, C.C. Teng, H.N. Yoon, Celanese Res.Co., 86 Morris Ave., Summit NJ 07901.

Currently available materials for NLO applications, such as optical modulation, routing, and amplification, lack many of the critical requirements for true industrial implementation. Inorganic and organic single crystals are difficult to grow, expensive, and are not capable of fabrication into intricate parts. Polymeric materials, on the other hand, can be manipulated into the desired orientation necessary for second or third order activity, fabricated into the desired shape, and the resultant structure frozen into place by cooling to room temperature (below  $T_g$ ). Structure-property relationship studies on a large number of small molecule organics have been conducted. The compounds with the highest molecular activity,  $B$ , were incorporated into polymeric structures to achieve materials with high second order susceptibility. These NLO polymers can now be fabricated into the desired orientation and shape for subsequent utilization in a variety of device applications.



● TUESDAY AFTERNOON - SECTION A - SYMPOSIUM ON ELECTROACTIVE POLYMERS  
- COSPONSORED WITH THE DIVISION OF POLYMER CHEMISTRY (CONTINUED) -  
H.F. King, Presiding

84. THEORETICAL STUDIES OF ELECTRONIC STATES AND DEFECTS IN CONJUGATED POLYMERS, Robert Silbey, Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.

We present semiempirical calculations of the electronic structure of conjugated polymers, such as the polydiacetylenes and polyaniline, in order to discuss the conductivity and optical properties of these systems. We will assess the role of defects in these systems.

85. ELECTRONIC TRANSPORT IN DISORDERED POLYMERIC FILMS.  
H. Scher, Standard Oil R&D Center, 4440 Warrensville Center Road, Cleveland, Ohio 44128

The study of electronic transport in a well investigated photoconducting polymer system has been revisited. Photocurrents in polyvinylcarbazole (PVK) were studied over 10 decades in time. An analytical approach is proposed for extracting rate distributions from the measured photocurrents which is completely general. We find that the trapping rate distribution is not exponential but 'flat' and that it shows a cutoff at low rates. This distribution gives rise to the novel feature of a gradual transition from dispersive to non-dispersive charge transport during a single transit. The temperature- and field dependence of the cutoff rate  $r_c$  was studied in the framework of a Poole-Frankel model. We discuss the generality of the results, resolution limitation of our analytic approach, the importance of measuring over many decades, and an interpretation of the mobility mechanism.

86. CONFORMATIONAL DEPENDENCE OF TRANSITION MOMENTS IN CONJUGATED POLYMERS. Z.G. Soos, Dept. of Chem, Princeton University, Princeton N.J. 08544; K.S. Schweizer, Sandia National Laboratories, Albuquerque, N.M. 87185

Both polydiacetylenes (PDAs) and polysilanes undergo rod-to-coil transitions that blue shift and broaden their lowest optical absorption. Such conformational effects are conventionally interpreted as breaks in the conjugation path that result in shorter segments with higher-energy absorptions. We demonstrate blue shifts in the opposite limit, when conjugation changes are neglected entirely, arising from conformational contributions to the transition moment. The total intensity satisfies a sum rule, is sharply peaked at the band gap for a rod, and is blue shifted in the coil on relaxing crystal selection rules in a wormlike polymer with persistence length  $(2a)^{-1}$ . Similar effects are attributed to the crystalline and amorphous regions of polyacetylene (PA). The correlation dependence of the absorption is considered in the exciton and electron-hole limits. At least part of the observed blue shifts have a simple conformational origin for persistence lengths of 5-10 bonds.

87. EXCITATIONS IN CONJUGATED POLYMERS, E.J. Mele and G.W. Hayden, Department of Physics, University of Pennsylvania, Philadelphia, PA 19104

A Hubbard-Peierls Hamiltonian is applied to study the spectrum of self localized excited states for several model conjugated polymers. We employ a numerical renormalization group method to study correlation effects in finite polyenes of intermediate length, and a more approximate configuration interaction scheme to extrapolate the results to longer systems. We find that a highly correlated even parity singlet excited state competes with an odd parity singlet excitation as the lowest singlet excitation, in agreement with various studies on the Pariser-Parr-Pople model. The lowest lying excitations in the model are identified as triplet excitations. Self consistently relaxed lattice configurations surrounding these electronic excitations are studied. Here we find a relaxation of the odd parity excited singlet into solitons in the bond alternation field, as well as a similar relaxation for the even parity excited state singlet. We demonstrate that correlations in the presence of the short range repulsive potential provides a mechanism for the production of long lived spin 1/2 neutral excitations for degenerate ground state systems and spin 1 neutral excitations for nondegenerate ground state polymers.

150. SOLUBLE HETEROAROMATIC LADDER POLYMERS: POLARONS AND ELECTRICAL CONDUCTIVITY. L. R. Dalton, J. Thomson, C. L. Young, L. P. Yu, P. H. Bryson, and R. Montgomery, Department of Chemistry, University of Southern California, Los Angeles, CA. 90089-0482.

Heteroaromatic ladder polymers of symmetry (i.e.,  $A=B$ ) sufficiently high to support polarons have been synthesized by condensation reactions employing monomers derivatized with various (including flexible chain) substituents. Not only are the resulting polymers soluble in conventional solvents but paramagnetic species are observed to be highly stable; and for shorter polymer segments, prepared by sequential synthesis techniques, resolved hyperfine interactions are observed in the conventional EPR spectra. Spin density distributions have been defined by analysis of the EPR spectra and by ENDOR measurements. Preparation of soluble polymers of defined chain length has permitted evaluation of the dependence of electron delocalization upon chain length which in turn provides insight into electrical conductivity and nonlinear optical activity in these materials. Intrinsic electrical conductivity measurements have been correlated with measurements of the optical gap for both solution and film samples. Cyclic voltammetry measurements have been executed to define oxidation/reduction potentials. Experimental parameters are correlated with theory.

151. TRANSPORT MODELS OF POLYACETYLENE: INSIGHTS FROM MAGNETIC RESONANCE EXPERIMENTS. M. Thomann and M. Jin, Exxon Research and Engineering, Route 22E, Annandale, NJ 08801; G. L. Baker, Bell Communications Research, 331 Newman Springs Road, Red Bank, NJ 07701; E. Hustedt and B. M. Robinson, Department of Chemistry, University of Washington, Seattle, WA 98195

Magnetic resonance has played a major role in probing soliton dynamics in  $(CH)_x$ . Unfortunately, a plethora of often conflicting conclusions have been reported for both the magnitude and temperature dependence of the diffusion rate as well as for the 1-D coherence length. One difficulty has been the intractable and disordered nature of  $(CH)_x$  prepared according to the standard Shirakawa procedure. We have addressed this problem by performing a variety of key magnetic resonance experiments on a new form of  $trans-(CH)_x$  containing an order of magnitude fewer spins. Using this material it is possible to discriminate between the relative contributions of spin dynamics and spatial diffusion that have complicated the interpretation of magnetic resonance experiments. We find that previous estimates for both the on-chain diffusion rate and 1-D coherence length have been drastically overestimated. The implications of these new findings on transport models of polyacetylene will be discussed.

152. ELECTRONIC STRUCTURE OF POLYPHENYLENE VINYLENE. F.E. Karasz, R.W. Lenz, and J. Obrzut, Dept. of Polymer Science, University of Massachusetts, Amherst, MA 01003

The electronic spectrum of thin films of undoped PPV shows three absorption bands with maxima at 6.12 eV, 5.36 eV and 3.09 eV. The first two are related to localized molecular states, and the broad band at 3.09 eV is related to exciton motion in the periodic structure of the PPV chain. The 3.069 eV energy for the lowest transition in PPV calculated by using an electronic vibrational exciton model is in good agreement with the observed 3.09 eV polymer band. The vibrationally coupled exciton is also evident from the sharpening of the polymer band observed at 77K. The spectrum of electrochemically doped film shows two additional absorption bands at 0.80 eV and 2.1 eV associated with a di-cation delocalized over approximately four polymer units and surrounded alternately by neutral sites. Since the di-cation has a quinoid structure the original PPV periodicity is broken and the exciton motion cannot be characterized by the PPV wave vector. As a result the polymer band selectively decays with the appearance of the two lowest electronic transitions from doubly charged sites.

153. TOWARD NEW ELECTRONIC STRUCTURES IN CRYSTALLOGRAPHICALLY ORDERED ELECTROACTIVE CONJUGATED POLYMERS D.J. Sandman, GTE Laboratories Incorporated, 40 Sylvan Road Waltham, MA 02234 and M.T. Jones, Department of Chemistry, University of Missouri-St. Louis, St. Louis, MO 63121

The polydiacetylenes(PDA), a class of electroactive materials which are fully ordered crystallographically, have attracted interest in recent years due to reports of high values of carrier mobility and third order nonlinear susceptibility. The latter are accompanied by subpicosecond response times at off-resonance wavelengths. PDA may also serve as sources of other types of delocalized electronic structures. The synthesis of a crystallographically ordered mixed polyacetylene(  $\{AC=CA-BC=CB\}$  ), where A= N-carbasoyl and B=Br, has been achieved via the solid state reaction of poly-1,6-di-N-carbasoyl-2,4-hexadiyne(DCH) and bromine. The reactivity of poly-1,1',6,6'-tetraphenyl-hexadiylenediamine(THD) is compared to that of poly-DCH, and the magnetic properties of the resultant materials, as studied by static susceptibility and electron spin resonance, are contrasted. The roles of side chain energy levels and conjugation defects are discussed in relation to the reactivity of poly-DCH and -THD and the properties of the resultant materials.

● WEDNESDAY AFTERNOON - SECTION A - SYMPOSIUM ON ELECTROACTIVE  
POLYMERS - COSPONSORED WITH THE DIVISION OF POLYMER CHEMISTRY  
(CONTINUED) - L. Davis, Presiding

146. SIDE CHAIN LIQUID CRYSTALLINE COPOLYMERS FOR NLO RESPONSE, Anselm C. Griffin and Amjad M. Bhatti, Departments of Chemistry & Polymer Science, University of Southern Mississippi, Hattiesburg, MS 39406. Box 5043, Southern Sta.

Side chain liquid crystalline polymers are attractive candidate materials for non-linear optical response. In an attempt to obtain such polymers exhibiting highly non-linear behavior we have synthesized several polyacrylate side chain polymers in which the pendent nlo/mesogenic moiety is designed to give a large change in dipole moment upon  $\pi$ -excitation. In particular we have used copolymers in which one comonomer contains a chiral unit while the other comonomer contains the nonlinear optical chromophore. Design, synthesis and characterization of the monomers will be described along with the details of polymerization. In addition the liquid crystalline properties of the polymers will be described.

This work was supported by the Air Force Office of Scientific Research (AFOSR-84-0249).

167. AROMATIC HETEROCYCLIC LIQUID CRYSTALLINE POLYMERS: SYNTHESIS, PROPERTIES, AND USE IN ELECTROOPTICS. Steven P. Bitler, James F. Wolfe, SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025

Organic materials offer major advantages over inorganic materials in the field of electrooptics by exhibiting an increase in processability, fabrication, response time, damage threshold, and nonresonant susceptibility. We are synthesizing materials based on poly(p-phenylenebenzobisthiazole) (PBT) or poly(p-phenylenebenzobisoxazole) (PBO) that will be useful in either second order processes (noncentrosymmetric structures) or third order processes (highly conjugated structures). The subject polymers are prepared as a liquid crystalline solution and are ideal candidates for use in electrooptics because of unsaturated backbones and high degrees of molecular alignment. The synthesis and characterization of model compounds, oligomers, and polymers will be discussed along with physical measurements relating them directly to other electrooptic materials.

168. SYNTHESIS OF ELECTROACTIVE POLYMERS, F. Mudl, Y. Ikenoue and A. Patil, Institute for Polymers and Organic Solids and Department of Physics, University of California, Santa Barbara, CA 93106

At this symposium talk, we will present our latest results on the smallest bandgap conducting polymers synthesized to date (0.6 eV). We will also present our latest results on our soluble, processable conducting polymers based on substituted thiophenes.

We achieved the record small bandgap by suitable substitution of our 1 eV conducting polymer, PITN, and processability by alkyl and alkanesulfonate substitution on the thiophene ring of polythiophenes.

169. ORIENTATIONALLY ORDERED ELECTRO-OPTIC MATERIALS. K. D. Singer, J. E. Sohn, and M. G. Kuzyk, AT&T Engineering Research Center, P. O. Box 900, Princeton, NJ 08540.

Electro-optic and optical parametric interactions in materials require that the material be non-centrosymmetric. This has led to a great deal of research in growing non-centrosymmetric crystals. However, it can be shown that a material need not be crystalline to be non-centrosymmetric. Poled liquid crystals and polymer glasses belong to this group. Such poled materials incorporating molecules possessing large molecular second-order nonlinear optical susceptibilities have been shown to possess substantial optical nonlinearities in the near-infrared. The physical mechanisms underlying poled polymer glasses and liquid crystals will be described, and recent results in the measurement of the second-harmonic and electro-optic coefficients will be presented. Also discussed will be issues relating to the potential device applications of poled orientationally ordered materials.

THURSDAY MORNING - SECTION A - SYMPOSIUM ON ELECTROACTIVE POLYMERS  
- COSPONSORED WITH THE DIVISION OF POLYMER CHEMISTRY (CONTINUED) -  
L. Dalton, Presiding

180. CONFORMATIONAL TRANSITIONS IN POLYDIACETYLENE SOLUTIONS. D. G. Peiffer, T. C. Chung, D. N. Schulz, P. K. Agarwal, R. T. Garner, M. W. Kim, and R. R. Chance, Corporate Research, Exxon Research and Engineering, Annandale, NJ 08801. Route 22 East, Clinton Twp.

Visible absorption, infrared absorption, Raman, nonlinear optical, and kinetic measurements are all strongly suggestive of a single-chain origin for the conformational transitions observed for polydiacetylenes in the solution phase, poly4RCMU and poly3BCMU being the prototypical examples. Intramolecular association between substituent groups on the polydiacetylene backbone has been assigned as the driving force for the transition; in the case of the RCMU polymers, hydrogen bonding provides the association mechanism. We report here rheological and time-temperature dependent quasielastic light scattering measurements for poly4BCMU in the dilute-semidilute regime. Light scattering measurements during the coil-to-rod transformation (yellow-to-red color change) demonstrate that dramatic color changes take place without any measurable change in hydrodynamic radius, confirming the single-chain origin of the conformational change. On aging, aggregation is observed as an order-of-magnitude increase in hydrodynamic radius. A parallel series of experiments on poly3BCMU is now underway.

181. ELECTRICALLY CONDUCTIVE POLYMERIC MATERIALS AND NONLINEAR OPTICAL MATERIALS BASED UPON POLY(p-PHENYLENEBENZOBISTHIAZOLE), PBT. P. DePra, J. G. Gaudiello, J. Giesler, D. Li, S. H. Carr, M. A. Ratner, and T. J. Marks, Dept. of Chemistry, Dept. of Materials Science and Engineering, and the Materials Research Center, Northwestern University, Evanston, IL 60201.

The rigid-rod ordered polymer poly(p-phenylenebenzobisthiazole), PBT, is one of the strongest and most robust man-made substances. In this lecture, we discuss research aimed at employing the unusual properties of PBT to produce new electrically conductive polymers and to produce new optical materials with highly nonlinear response. Strong, processable, PBT-based conductive materials can be synthesized by "alloying" PBT with phthalocyanine molecular metals. We report on the microstructure, charge transport characteristics, thermal, and mechanical properties of fibers produced from such alloys. In addition, films of pure PBT can be doped electrochemically to produce electrically conductive polymeric materials. The electrochemical, structural, optical, and charge transport properties of these films are discussed. Finally, PBT can be employed as a matrix in "guest-host" approaches to nonlinear optical materials. The choice of host material is guided by highly accurate, computationally efficient, PPP  $\pi$ -electron calculations of molecular optical nonlinearities.

182. THERMODYNAMIC STUDY OF ELECTRON-HOLE EQUILIBRIA IN ELECTROACTIVE POLYMERS. Howard Reiss and Dai-uk Kim, Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024.

The equilibrium distribution of an electroactive dopant between a polymer and an external phase depends on the "ionization equilibria" involving electrons, holes, polarons, bipolarons, etc. within the polymer. This is amply demonstrated in semiconductors. Thus, thermodynamic measurements on the distribution have information on band structure and mechanisms of ionization. Furthermore these data are free of complications associated with "interchain hopping". We have undertaken such measurements concurrent with conventional ones, for the system iodine vapor-polythiophene. Reversible absorption and conductivity measurements reveal remarkable phenomena, including (in the case of films) a sharp discontinuity to saturation, depending only on total pressure, and probably of electromechanical origin. Its explanation may involve the formation of Schottky diode between the film and its gold substrate, or changes accompanying the merging of filled and empty bipolaron bands. The phenomenon is absent in free standing polythiophene powders. The absorption isotherms at low iodine pressures reveal information on electronic equilibria.

183. POLED POLY(VINYLDENE FLUORIDE) AS A HOST FOR GUEST NON-LINEAR OPTICAL MOLECULES. P. Pantelis, J. R. Hill and G. J. Davies, British Telecom Research Laboratories, Martlesham Heath, Ipswich, IP5 7RE, United Kingdom.

Incorporating guest non-linear molecules into polymeric hosts is an attractive technique as it offers the opportunity of utilising highly non-linear species which might otherwise crystallise centrosymmetrically. These molecules require ordering in their host by the application of electric fields (poling). Often, this is not achievable owing to dielectric breakdown or bulk conductivity. However, it is known from our earlier piezoelectric work that a copolymer of vinylidene fluoride and trifluoroethylene can sustain intense electric fields. This, together with the accompanying dipolar ordering of the polymer crystallites should produce a host material with a stable, high, internal residual electric field. We have measured internal fields as high as  $1.4 \times 10^6$  Vm<sup>-1</sup>. The residual field should then maintain the alignment of guest non-linear molecules and produce a stable system. Processing details are given, including film-formation by solvent casting and corona poling. Results on film characterisation are also included.

● THURSDAY AFTERNOON - SECTION A - SYMPOSIUM ON ELECTROACTIVE  
POLYMERS - COSPONSORED WITH THE DIVISION OF POLYMER CHEMISTRY  
(CONTINUED) - P.N. Prasad, Presiding

190. ELECTRO-OPTIC DEVICE APPLICATIONS OF POLYMER LIQUID CRYSTALS. Harry J. Coles,  
Liquid Crystal Group, Physics Department, The University, Manchester M13 9PL, U.K.

Over the past few years developments in polymer synthesis have led to a new class of orientable liquid crystal polymers with considerable potential for electro- and opto-optic device applications. These polymers have flexible or semi-flexible backbones with pendant electro-active side chain mesogens. In this talk we will discuss the structural features that lead to and control the liquid crystalline properties of such polymers. We will show how these materials may be aligned in electrical and optical fields and how the degree of alignment may be reproducibly controlled and stored. Experimental data from light scattering, birefringence, dielectric dispersion, viscosity and electro-optic response time measurements will be presented. By attaching optically anisotropic dichroic, fluorescent or optically non linear side groups to the polymers a new range of optical phenomena have been recorded and these will be discussed in terms of novel device applications.

191. NONLINEAR AND ELECTRO-OPTIC ORGANIC DEVICES. R. Lytel, G.F. Lipscomb, and J.I. Thackara, Lockheed Research and Development Division, 0/97-20, B/202, 3251 Manover Street, Palo Alto, California 94304

Organic and polymeric materials have emerged in recent years as a promising class of nonlinear optical media for novel device applications. The nonresonant interaction of light with the  $\pi$ -electron system in certain organic materials leads to the possibility of fabricating faster, more efficient devices than with inorganic media. Major benefits of these materials include large, ultrafast susceptibilities, low DC dielectric constants, and significant structural and optical features, such as architectural flexibility (films, crystals), high optical damage thresholds, broadband visible response, and stability. We present an overview of the nonlinear optics of select organic materials at picosecond time scales and describe recent progress in the fabrication of waveguide electro-optic devices based on polymer films.

192. NON-LINEAR OPTICAL PROCESSES IN OPTICAL FIBRES. B. K. Mayar, British Telecom Research Laboratories, Martlesham Heath, Ipswich IP5 7RE, United Kingdom.

Advances in the development of highly non-linear organic materials have stimulated interest in the fabrication of optical parametric devices. Optical fibres with non-linear organic crystalline cores are becoming increasingly popular as they afford protection to the organic cores and have the advantage of uniform dimensions for phase-matching. They are also compatible with silica fibres. The fabrication process involves orientated crystal growth from the melt within glass capillaries. A number of materials have been successfully grown in capillaries with 2  $\mu$ m to 10  $\mu$ m bore diameters and upto 50mm lengths for single mode operation. At the meeting, fabrication, assessment of linear and non-linear optical properties of crystal cored fibres, and device design constraints will be discussed.

193. NONLINEAR OPTICAL PROCESSES AND APPLICATIONS IN THE NEAR AND FAR INFRARED SPECTRAL REGION WITH LIQUID CRYSTALS. J. C. KHOO, Department of Electrical Engineering, Pennsylvania State University, University Park, PA. 16802

Nematic liquid crystals are generally quite transparent throughout the infrared region. This property, in combination with their extremely large room temperature optical nonlinearity, and our recent success in fabricating millimeter thick nematic films, make them excellent candidates for novel nonlinear optics applications. In particular, optical beam and image amplifications, optical phase conjugation and intensity switching processes can be performed with relatively low power CO<sub>2</sub> and CO lasers. I will discuss the theories and some new aspects of these nonlinear processes, the roles played by the liquid crystal films and recently obtained experimental results. Special geometrical and optical configurations governing the success of these processes, the power and intensity requirements, response times and the efficiencies of these processes will also be presented.

● FRIDAY MORNING - SECTION A - SYMPOSIUM ON ELECTROACTIVE POLYMERS  
 - COSPONSORED WITH THE DIVISION OF POLYMER CHEMISTRY (CONCLUDED)  
 - G.L. Baker, Presiding

201. NEW SYNTHETIC ROUTES FOR NOVEL ELECTROACTIVE POLYMERS. J. Thomson and L. R. Dalton, Department of Chemistry, University of Southern California, Los Angeles, CA 90089.

A major impediment to the application of so-called "conducting polymers" has been their insolubility. We have addressed this problem of processibility by synthesizing soluble precursor polymers such as Durham polyacetylene and by preparing derivatized monomers which when used in condensation reactions lead to soluble electroactive polymers. We have also developed sequential synthesis techniques, including the use of blocking and end-capping reagents, which have permitted preparation of polymers of defined chain length. Control of chain length and morphology is important for defining the mechanisms of nonlinear optical activity and electrical conductivity and for optimizing such activity. The preparation of soluble polymers has also facilitated post polymerization derivatization, copolymer preparation, and composite fabrication.

202. POLYQUINOLINE BASED INTRINSIC CONDUCTING POLYMERS. L. Y. Chiang, D. C. Johnston, and J. P. Stokes, Corporate Research Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey 08801 Route 22 East.

A series of quinoline oligomers were synthesized by a novel catalytic dehydrogenative polymerization of tetrahydroquinoline using rhenium sulfide as a catalyst. The vapour phase thermolysis of these quinoline oligomers at 900 - 1000°C yields a new class of highly intrinsic conducting organic polymer films. Both transmission electron microscopy and powder x-ray diffraction of the film showed an amorphous structureless appearance without any obvious evidence for graphitic layer structure. These films exhibit a conductivity of higher than 400 S/cm at room temperature without doping and a good stability under ambient condition. The conductivity was found to be very weakly temperature dependent, as in a metal, with a resistance ratio of  $R_{29\text{ K}}/R_{300\text{ K}}$  equal to only 1.41, and a resistance maximum at 29 K. We report also the results from the thermopower measurements.

203. PROPERTIES OF LOW SPIN DENSITY TRANS-POLYACETYLENE. Gregory L. Baker, John A. Shelburne III, and Shahab Etemad, Bell Communications Research, 331 Newman Springs Road, Red Bank NJ 07701; Hans Thomann, Exxon Research and Engineering, Route 22, Annandale, NJ 08801; Lewis Rothberg, AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974.

*Trans*-polyacetylene containing an order of magnitude fewer spins than standard samples can be prepared by a modification of the Shirakawa procedure for polyacetylene synthesis. This material is identical to Shirakawa *trans*-polyacetylene except for properties which depend upon the spin density. Magnetic resonance experiments indicate that the neutral defects in the low spin material are chemically identical to those in Shirakawa samples, yet are immobile. In photoinduced absorption experiments, spectral features observed at microsecond time delays which have been attributed to charged solitons are found to be strongly correlated with the spin density. These results help clarify the optical and magnetic properties of *trans*-polyacetylene.

204. TOWARDS UNDERSTANDING ENERGY GAPS OF CONJUGATED POLYMERS. Miklos Kertesz and Y.S. Lee, Department of Chemistry, Georgetown University, Washington, DC 20057.

The electronic structure of polymers with aromatic (A) and quinoid (Q) forms are reviewed (polypyrrole, poly-p-phenylene, polythiophenes, etc.) based on recent more reliable MNDO polymer geometry optimized total energy calculations. Polythiophenes with bridging -CPh- groups

have been found by Jenekhe to possess as small energy gaps as half of that of polyacetylene ( $-\text{CH}=\text{CH}-$ ), PA. It is found, that the bond length alternation along the C-C backbone of the polymer is similar to, but modified relative to, that of PA. The presence of A and Q groups is a consequence of the fact, that an odd number of  $-\text{CR}=\text{}$  groups bridges the two types of rings. For  $x=y$  the hetero-substitution has no significant effect on the gap, if needed the experimental results can be described well. The trends for the case of  $x \neq y$  and several other S and N substituted polymers are also discussed.

205. OFF RESONANCE, ELECTRONIC  $\chi^{(3)}$  IN CONJUGATED POLYMERS

Shahab Etemad, Francois Kajzar, and Gregory L. Baker,  
Bell Communications Research, Red Bank, NJ 07701.  
\* Also at CEA-IRDA, CEN/Saclay, 91191 Gif-sur-Yvette, France.

Recently we reported the first quantitative measurement of  $\chi^{(3)}$  in polyacetylene through the third harmonic generation technique. We found the magnitude of  $\chi^{(3)}$  in the transparent gap region is in excess of  $10^{-9}$  esu and discovered the two-photon absorption band at 1.3  $\mu\text{m}$ . We found both the magnitude and the spectrum of  $\chi^{(3)}$  to be in agreement with the predictions of free electron band picture. Whereas the large value of  $\chi^{(3)}$  in polyacetylene has subsequently been confirmed, alternative theory based on the expected strong electron-phonon coupling has been invoked in order to explain the result. In this work we present new measurements from both polyacetylene thin films and single crystals of polydiacetylene (PTS). We have extended the long wavelength limit of our previous report upto about 4  $\mu\text{m}$  with the hope of reaching the true off resonance limit for both the fundamental and the third harmonic. These results will be discussed in an effort to determine the origin of the large  $\chi^{(3)}$  in conjugated polymers.

206. ELECTROCHEMISTRY OF POLYANILINE. Walter W. Focke and Gary Wnek, Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.

The conductivity and electrochemical behavior of electrochemically synthesized polyaniline films, in contact with aqueous electrolytes, were studied in the range  $0.4 < \text{pH} < 6$ . Cyclic voltammetry data indicate the presence of three redox processes. The positions of the oxidation and reduction peaks were found to vary with scan rate. Estimates for formal potentials were obtained by extrapolation to zero scan rate. For the first redox process, the formal potential ( $E_f = 0.05$  V vs SCE), is independent of pH. The formal potentials for the second and third redox processes shift to more cathodic potentials at rates between 80 and 120 mV/pH. The conductivity, at a given pH, shows a maximum at a potential roughly halfway between the formal potentials of the first and second redox processes. This optimum potential shifts to more cathodic potentials at a rate of  $\sim 70$  mV/pH. Potentiometric titration data show that the locus of optimum potential does not correspond to a unique redox state of the polymer. The implications of these observations on the conductivity mechanism in polyaniline will be discussed.

207. SPECTRO-ELECTROCHEMICAL STUDY OF POLYANILINE. R. J. Cushman, S. C. Yang and P. M. McManus, Department of Chemistry, University of Rhode Island, Kingston, RI 02881

Optical absorption spectra of polyaniline in the visible, near IR and IR spectral regions were measured with in-situ control of the electrochemical potential. The electrochemically induced electronic structural changes of polyaniline were found to be strongly dependent on the extent of protonation at the nitrogen atom sites. In-situ IR and Raman spectra provide information about the bonding and conformational changes when the electronic structure is switched. We will discuss the relation between the protonic acid doping and the electrochemical doping of polyaniline.

The electrical conductivity switching and the electrode activity changes of thin film polyaniline is correlated with the spectro-electrochemically determined transformations.

Support by NSF Grant CHE-8216482 is acknowledged.

208. ELECTROCHEMILUMINESCENCE AND CONDUCTION AT CHEMICALLY MODIFIED MICROELECTRODE ARRAYS. C.R. Cabrera, H.D. Abruna. Department of Chemistry, Cornell University, Ithaca, NY 14853.

Electrochemiluminescence and redox conduction studies at surface modified micro-electrode arrays will be presented. We have prepared, via electron beam micro-fabrication techniques, microelectrode arrays with four platinum electrodes that are 60  $\mu$ m long, 0.5  $\mu$ m in width with a 1.0  $\mu$ m interelectrode spacing.

The arrays were modified with electropolymerized layers of  $[m(v-bpy)_3]^{2+}$  ( $m=Fe, Ru, Os$ ;  $v-bpy$  is 4-vinyl 4-methyl 2,2'-bipyridine). Electrochemiluminescence was observed for electrodes modified with the ruthenium polymer. Redox conduction studies were carried out on homopolymer and on copolymer films.

209. SYNTHESIS AND CONDUCTIVITY OF POLYMERIC TRANSITION METAL COMPLEXES COORDINATED BY DIAMINOBENZENEDITHIOL. Oh-Kil Kim, David McDermott and Tsong Tsai, Naval Research Laboratory, Washington, D. C. 20375-5000 Code 6120.

Linear coordination polymers of transition metals were prepared from metal (II) halides and a tetradentate ligand, 1,4-diamino-2,5-benzenedithiol, under aqueous alkaline conditions free of oxygen. The resulting polymeric metal complexes are black-colored insoluble powders. The stoichiometry of the metal relative to the ligand is 1.25 - 1.50. The X-ray diffraction shows these metal-complexed polymers to be crystalline and their diffraction patterns are almost all identical, while their peak positions are shifted to higher diffraction angles as their electrical conductivity increases. The room temperature conductivity of compaction samples of the complexed polymers is highest with the Co-complex ( $2.1 \times 10^{-1}$  S/cm) and is least with the Ni-complex ( $1.9 \times 10^{-6}$  S/cm). Those of Fe- and Cu-complexes are  $1.0 \times 10^{-2}$  and  $5.4 \times 10^{-6}$  S/cm, respectively. These metal-complexed polymers exhibited paramagnetic behavior, and the polymer conductivity was found to be proportional to the spin density and linewidth of ESR spectra.



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